$Ta_{1\cdot091}O_3$ per unit cell, *viz.* 7·4 g.cm^{-3}, rather than with that for anion vacancies.

We obtained powder patterns of KTa_5O_{13} which we could not index, but attempts to grow crystals by cooling melts from 1700 °C in iridium led to solid solutions of potassium oxide in high-temperature tantala.

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Computational Aspects of Space-Group Symmetry

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Some well-known results which are often used in the analysis of X-ray diffraction data are derived, and some new results proved. Algorithms are given which allow these results to be used on a computer.

Introduction

In recent papers Jeffery (1963) and Bienenstock & Ewald (1962) have studied the symmetry of reciprocal space; earlier work by Buerger (1949), Waser (1955) and Trueblood (1956) has dealt with other aspects of the effects of symmetry on X-ray diffraction. In this paper, an attempt is made to develop a systematic approach to the problems arising in programming a digital computer for the three basic calculations of crystallography, *i.e.* structure factors, Fourier synthesis and least squares. Some of the results have been derived by earlier workers; some, to the best of the writer's knowledge, have never been derived at all, although they are in common use; still others are new. In each case, algorithms for application of the results are given, in ALGOL 60 reference language (Naur, 1963).

Notation

We shall denote a group by a script capital, *e. g.* $\mathscr{G}, \mathscr{H}$, and particular elements of a group by upper case letters, possibly with a suffix, *e.g.* G, H_i. Since the groups with which we are concerned are all groups of symmetry operations, it is convenient to describe them in terms of matrices; in particular a bold-faced $\mathbf{R}$ denotes a 3×3 rotation matrix each of whose elements is either $+1$, 0 or -1, and $\mathbf{t}$ denotes a 3×1 matrix (column vector) whose elements are all multiples of $\frac{1}{12}$ and lie in the range 0 to <1. The inverse of $\mathbf{R}$ is written $\mathbf{R}^{-1}$ and its transpose as $\mathbf{R}^t$.

The action of any crystallographic symmetry operator G, on a vector $\mathbf{r}$ can be defined as

$$G\mathbf{r}=\mathbf{R}\mathbf{r}+\mathbf{t} \qquad (1\cdot1)$$

i.e. as rotation followed by a translation. The result is a new vector, and it is understood that each element of the result is normalized to lie in the range 0 to <1.

Following Lomont (1959), we shall find it convenient to use the notation

$$G\mathbf{r}=\mathbf{R}\mathbf{r}+\mathbf{t}=(\mathbf{R}|\mathbf{t})\mathbf{r} \tag{1·2a}$$

or

$$G\equiv(\mathbf{R}|\mathbf{t})\,. \tag{1·2b}$$

Every space group contains a unit element U, which has the property that for any $\mathbf{r}$

$$U\mathbf{r}=(\mathbf{U}|\mathbf{u})\mathbf{r}=\mathbf{r}\,. \tag{1·3a}$$

Obviously $\mathbf{U}=\mathbf{I}$ the unit matrix, $\mathbf{u}=\mathbf{0}$ the null vector, and

$$U\equiv(\mathbf{I}|\mathbf{0})\,. \tag{1·3b}$$

The product of two operators G_1G_2 is defined by

$$G_1G_2\mathbf{r}=(\mathbf{R}|\mathbf{t})_1\,(\mathbf{R}|\mathbf{t})_2\,\mathbf{r} \tag{1·4a}$$

$$=(\mathbf{R}|\mathbf{t})_1\,(\mathbf{R}_2\mathbf{r}+\mathbf{t}_2) \tag{1·4b}$$

$$=\mathbf{R}_1\mathbf{R}_2\mathbf{r}+\mathbf{R}_1\mathbf{t}_2+\mathbf{t}_1 \tag{1·4c}$$

from which we deduce that

$$G_1G_2\equiv(\mathbf{R}|\mathbf{t})_1\,(\mathbf{R}|\mathbf{t})_2\equiv(\mathbf{R}_1\mathbf{R}_2|\mathbf{R}_1\mathbf{t}_2+\mathbf{t}_1)\,. \tag{1·4d}$$

Comparison of (1·4*d*) and (1·3*b*) shows that if G_2 is the inverse of G_1, *i.e.* if

$$G_1G_2\equiv U\,,$$

then

$$\mathbf{R}_1\mathbf{R}_2=\mathbf{I}\quad \textit{i.e.}\ \mathbf{R}_2=\mathbf{R}_1^{-1} \tag{1·5a}$$

and

$$\mathbf{R}_1\mathbf{t}_2+\mathbf{t}_1=\mathbf{0}\quad \textit{i.e.}\ \mathbf{t}_2=-\mathbf{R}_1^{-1}\mathbf{t}_1 \tag{1·5b}$$

so that

$$(\mathbf{R}|\mathbf{t})_1^{-1}\equiv(\mathbf{R}_1^{-1}|-\mathbf{R}_1^{-1}\mathbf{t}_1) \tag{1·5c}$$

Direct space symmetry

General positions

Let $\mathcal{G}$ be a space group, of order g. Then if $\mathbf{r}$ is an arbitrary position in the unit cell, it is in general true that

$$G_1\mathbf{r}\neq G_2\mathbf{r}\neq\dots G_{g-1}\mathbf{r}\neq G_g\mathbf{r} \tag{2·1}$$

i.e. the result of applying the elements of $\mathcal{G}$ in turn to the position $\mathbf{r}$ is to give in all g distinct but related positions. If this is so we speak of $\mathbf{r}$ as being a 'general position' in the unit cell, and of the positions $G_i\mathbf{r}$ $(1\le i\le g)$ as being 'equivalent' to the position $\mathbf{r}$.

Special positions

In some space groups there are certain positions $\mathbf{s}$ in the unit cell for which

$$G_p\mathbf{s}=G_q\mathbf{s}=\dots G_r\mathbf{s}\ (h\ \text{suffices})\,, \tag{2·2}$$

i.e. the result of applying h different elements of $\mathcal{G}$ in turn to the position $\mathbf{s}$ is to give the same position h times over. In this case we call $\mathbf{s}$ a 'special position'.

Multiply equations (2·2) by the inverse of any element: without any loss in generality we choose G_r^{-1}. Then

$$G_r^{-1}G_p\mathbf{s}=G_r^{-1}G_q\mathbf{s}=\dots G_r^{-1}G_r\mathbf{s}=\mathbf{s} \tag{2·3a}$$

or

$$G_{p'}\,\mathbf{s}=G_{q'}\,\mathbf{s}=\dots=U\mathbf{s} \tag{2·3b}$$

where

$$G_{q'}\equiv G_r^{-1}G_p. \tag{2·4}$$

The h elements appearing in (2·2) are distinct, and so therefore are the elements in (2·3); further the complex of elements in (2·3) is closed, as may be simply demonstrated by multiplying (2·3*b*) by any element appearing in the complex. This complex is therefore a subgroup of $\mathcal{G}$, of order h; let us call it $\mathcal{H}$. The order of $\mathcal{H}$ is a factor of g, the order of $\mathcal{G}$; suppose $n=g/h$. Then we can express $\mathcal{G}$ in the form

$$\mathcal{G}=\mathcal{H}G_1+\mathcal{H}G_2+\dots\mathcal{H}G_n \tag{2·5}$$

where $G_1, G_2\dots G_n$ are any n elements of $\mathcal{G}$ which satisfy the condition

$$G_1\mathbf{s}\neq G_2\mathbf{s}\neq\dots G_n\mathbf{s}\,. \tag{2·6}$$

These results allow us to replace an atom which occurs in a special position $\mathbf{s}$, by a 'fractional' atom, whose scattering power is $1/h$ of that of the atom which actually occurs there, and then to treat the atom as though it were in a general position. An alternative approach is described by the ALGOL procedure 'Load cell' in the Appendix. This is an algorithm which, given a table of the contents of the asymmetric unit of a structure, and a table of the elements of the space group, will enumerate the contents of the unit cell, giving each atom its correct multiplicity. A by-product of this process is a table showing which group elements give rise to a particular atom. We now show how this information may be used to find what restrictions are imposed on the coordinates and thermal parameters of atoms on special positions.

Restrictions on coordinates

An atom in a special position satisfies equations (2·2), which imply (2·3*b*). A necessary and sufficient condition that $\mathbf{s}$ shall satisfy (2·3*b*) is that it may be expressed in the form

$$\mathbf{s}=1/h\sum_{\mathcal{H}}G_{p'}\mathbf{r} \tag{2·7}$$

where the summation is over the elements of the subgroup $\mathcal{H}$. The condition is readly seen to be sufficient by direct substitution of (2·7) in (2·3*b*); in each case the resulting summation is a reordering of the same terms. The condition is necessary, for addition of the h separate equations

$$\mathbf{s}=G_{p'}\mathbf{s}$$

leads directly to (2·7).

Restrictions on thermal parameters

An atom in a special position also has restrictions on the values of its thermal parameters. The scattering by an atom which is undergoing anisotropic thermal motion is usually described by forming the convolute of the electron density of the stationary atom with a probability density; the Fourier transform of this leads to a reduction of the scattering power of the atom by a factor

$$\varphi = \exp - \mathbf{h}^t \mathbf{T} \mathbf{h} \qquad (2\cdot 8)$$

where $\mathbf{T}$ is a symmetric positive definite matrix of order 3, the vibration matrix, and $\mathbf{h}$ the reciprocal lattice point at which the scattering is observed. For an atom on a general position the value of $\mathbf{T}$ is arbitrary: let us write it in the form

$$\mathbf{T} = \sum_{i=1}^{3} \mathbf{e}_i \lambda_i \mathbf{e}_i^t \qquad (2\cdot 9)$$

where λ_i is an eigenvalue of $\mathbf{T}$ and $\mathbf{e}_i$ the associated eigenvector. When an operator G_p is applied to the atom, the coordinates are transformed, and the value of $\mathbf{T}$ is also transformed, to $\mathbf{T}_p$. The eigenvalues of $\mathbf{T}$ are unaltered, but the eigenvectors are transformed to

$$\mathbf{e}_i' = \mathbf{R}_p \mathbf{e}_i \,. \qquad (2\cdot 10)$$

The transformed value of $\mathbf{T}$ is then

$$\mathbf{T}_p = \sum_{i=1}^{3} \mathbf{e}_i' \lambda_i \mathbf{e}_i'^t \qquad (2\cdot 11a)$$

$$= \sum_{i=1}^{3} \mathbf{R}_p \mathbf{e}_i \lambda_i \mathbf{e}_i^t \mathbf{R}_i'^t \qquad (2\cdot 11b)$$

$$= \mathbf{R}_p \mathbf{T} \mathbf{R}_p^t \,. \qquad (2\cdot 11c)$$

If the atom is in a special position, then (2·11*c*) still holds. There is now a restriction that $\mathbf{T}$, the vibration matrix, shall transform into itself under each element of $\mathscr{H}$, so that

$$\mathbf{T} = \mathbf{R}_{p'} \mathbf{T} \mathbf{R}_{p'}^t = \mathbf{R}_{q'} \mathbf{T} \mathbf{R}_{q'}^t = \ldots (h \text{ suffices}) \,. \qquad (2\cdot 12)$$

A necessary and sufficient condition is that $\mathbf{T}$ may be expressed in the form

$$\mathbf{T} = 1/h \sum_{\mathscr{H}} \mathbf{R}_{p'} \mathbf{S} \mathbf{R}_{p'}^t \qquad (2\cdot 13)$$

where $\mathbf{S}$ is a symmetric positive definite matrix, and the summation is over the elements of the subgroup $\mathscr{H}$. The proof of this is similar to that for the corresponding statement concerning coordinates. These results are a generalization of those of Trueblood (1956).

Reciprocal space symmetry

The structure factor $F(\mathbf{h})$ for a given reciprocal lattice point $\mathbf{h}$ may be written

$$F(\mathbf{h}) = \int_\tau \varrho(\mathbf{r}) \exp 2\pi i \mathbf{h}^t \mathbf{r} d\tau \qquad (3\cdot 1a)$$

where τ is the volume of a single unit cell, and $\mathbf{r}$ is the position of the volume element $d\tau$ within which the electron density is $\varrho(\mathbf{r})$. If we replace $\mathbf{r}$ by $G\mathbf{r}$ in (3·1*a*) the value of the integral is unaltered, *i.e.*

$$F(\mathbf{h}) = \int_\tau \varrho(G\mathbf{r}) \exp 2\pi i \mathbf{h}^t G \mathbf{r} d\tau \,. \qquad (3\cdot 1b)$$

Now

$$\varrho(G\mathbf{r}) = \varrho(\mathbf{r}) \,, \qquad (3\cdot 2)$$

the effect of G being to map the contents of the unit cell on to itself and

$$\mathbf{h}^t G \mathbf{r} = \mathbf{h}^t (\mathbf{R}|\mathbf{t})\mathbf{r} = \mathbf{h}^t \mathbf{R} \mathbf{r} + \mathbf{h}^t \mathbf{t} \,. \qquad (3\cdot 3)$$

Using (3·2), and (3·3) in (3·1*b*), and noting that

$$\mathbf{h}^t \mathbf{R} = (\mathbf{R}^t \mathbf{h})^t \qquad (3\cdot 4)$$

we find

$$F(\mathbf{h}) = \int_\tau \varrho(\mathbf{r}) \exp 2\pi i \{(\mathbf{R}^t\mathbf{h})^t \mathbf{r} + \mathbf{h}^t \mathbf{t}\} d\tau \,. \qquad (3\cdot 5a)$$

i.e.

$$F(\mathbf{h}) = \exp 2\pi i \mathbf{h}^t \mathbf{t} \int_\tau \varrho(\mathbf{r}) \exp 2\pi i (\mathbf{R}^t \mathbf{h})^t \mathbf{r} d\tau \qquad (3\cdot 5b)$$

on bringing the constant factor $\exp 2\pi i \mathbf{h}^t \mathbf{t}$ outside the integration. By comparison with (3·1*a*), the integral is seen to be simply $F(\mathbf{R}^t\mathbf{h})$ and we have the important result

$$F(\mathbf{h}) = \exp 2\pi i \mathbf{h}^t \mathbf{t} \, F(\mathbf{R}^t \mathbf{h}) \qquad (3\cdot 6a)$$

or

$$F(\mathbf{R}^t \mathbf{h}) = \exp -2\pi i \mathbf{h}^t \mathbf{t} \, F(\mathbf{h}) \,. \qquad (3\cdot 6b)$$

This result was derived by Waser (1955).

Lattice absences

An important complex of $\mathscr{G}$ is that for which $\mathbf{R}$ is equal to the unit matrix, *i.e.* those elements of the form

$$G_i \equiv (\mathbf{I}|\mathbf{t}_i) \,. \qquad (3\cdot 7)$$

Obviously this complex forms a subgroup of $\mathscr{G}$, for if G_i, G_j are any two elements then (1·4*d*) shows that their product is

$$G_i G_j \equiv (\mathbf{I}|\mathbf{t}_i)\,(\mathbf{I}|\mathbf{t}_j) \equiv (\mathbf{I}|\mathbf{t}_i + \mathbf{t}_j) \,, \qquad (3\cdot 8)$$

which is of the form (3·7), the complex therefore being closed. We thus have a subgroup each of whose elements is simply a translation; note that such a subgroup cannot give rise to a special position, for there is no non-trivial value of $\mathbf{t}$ such that

$$(\mathbf{I}|\mathbf{t})\mathbf{r} = \mathbf{r} + \mathbf{t} = \mathbf{r} \,.$$

We shall denote this subgroup by $\mathscr{E}$ and its order by e. The inverse of any element in $\mathscr{E}$, say $(\mathbf{I}|\mathbf{t}_i)$ is, from (1·5*c*), the element

$$(\mathbf{I}|\mathbf{t})_i^{-1} \equiv (\mathbf{I}|-\mathbf{t}_i) \,. \qquad (3\cdot 9)$$

Thus, for any element E_i there is an element $E_{i'}$, with the property that

$$\exp 2\pi i \mathbf{h}^t \mathbf{t}_i = (\exp 2\pi i \mathbf{h}^t \mathbf{t}_{i'})^* \,. \qquad (3\cdot 10)$$

(In some cases the element $E_{i'}$ may be E_i itself. This implies that

$$\mathbf{t}_i \equiv -\mathbf{t}_i \quad (\text{mod } 1) \,, \qquad (3\cdot 11)$$

i.e. that the elements of $\mathbf{t}_i$ are all either 0 or $\frac{1}{2}$).

Consider the sum of all the equations (3·6*a*) which are produced by the subgroup $\mathscr{E}$; there are e such equations and we find

$$\mathbf{e}F(\mathbf{h})=F(\mathbf{I}^t\mathbf{h})\sum_{\mathscr{E}}\exp 2\pi i\mathbf{h}^t\mathbf{t}_i\,. \tag{3·12}$$

Bearing 3·10 in mind, the value of the summation is some real number; thus if the real number k is defined by

$$k=\sum_{\mathscr{E}}\exp 2\pi i\mathbf{h}^t\mathbf{t}_i \tag{3·13}$$

then 3·12 is

$$\mathbf{e}F(\mathbf{h})=kF(\mathbf{h})\,. \tag{3·14}$$

There are now two possibilities

(1) $e=k$, and $F(\mathbf{h})$ is arbitrary
(2) $e\neq k$, and hence $F(\mathbf{h})$ is identically zero.

The values of $\mathbf{h}$ for which $F(\mathbf{h})$ is thus constrained to be zero are the 'lattice absences'.

The subgroup $\mathscr{E}$ has the property that for any element G in $\mathscr{G}$,

$$G^{-1}\mathscr{E}G=\mathscr{E}\,. \tag{3·15}$$

(This is most easily verified by evaluating a typical triple product.)

The subgroup $\mathscr{E}$ is thus a normal subgroup of $\mathscr{G}$, and we can form the quotient group $\mathscr{H}$, with order $h(=g/e)$ defined by

$$\mathscr{G}=\mathscr{E}H_1+\mathscr{E}H_2+\ldots\mathscr{E}H_h\,. \tag{3·16}$$

The implication is that it is possible to separate out completely the effects of the lattice translations when discussing diffraction phenomena. The translation group $\mathscr{E}$ causes some reflexions to be completely absent: others are present and the structure factors are simply e times those which would be generated by the group $\mathscr{H}$ acting on the asymmetric unit. The remainder of this section is concerned solely with the group $\mathscr{H}$, defined by (3·16).

Space-group absences

Consider the set of h equations which are the result of applying the elements of $\mathscr{H}$ in (3·6*b*).

$$F(\mathbf{R}_i^t\mathbf{h})=F(\mathbf{h})\exp-2\pi i\mathbf{h}^t\mathbf{t}_i \qquad 1\leq i\leq h\,.$$

In general, the products $\mathbf{R}_i^t\mathbf{h}$ are not equal; there will however be certain values of $\mathbf{h}$ for which there are equations of the form

$$\mathbf{R}_i^t\mathbf{h}=\mathbf{R}_j^t\mathbf{h}=\ldots\mathbf{R}_k^t\mathbf{h}\quad(p\text{ suffices}) \tag{3·17a}$$

analogous to equations (2·2). Obviously there exists a subgroup of $\mathscr{H}$, which is defined by

$$\mathbf{R}_{i'}^t\mathbf{h}=\mathbf{R}_{j'}^t\mathbf{h}=\ldots\mathbf{R}_{k'}^t\mathbf{h}=\mathbf{h}\,, \tag{3·17b}$$

where

$$\mathbf{R}_{i'}=\mathbf{R}_i\mathbf{R}_k^{-1}\,. \tag{3·18}$$

If we now examine the sum of equations (3·6*b*) for the elements of this subgroup we find

$$pF(\mathbf{h})=pF(\mathbf{R}_i^t\mathbf{h})=F(\mathbf{h})\sum_{\mathscr{H}}\exp(-2\pi i\mathbf{h}^t\mathbf{t}_i)\,. \tag{3·19}$$

The inverse of any element (equation 1·5*c*) is

$$(\mathbf{R}|\mathbf{t})_i^{-1}\equiv(\mathbf{R}_i^{-1}|-\mathbf{R}_i^{-1}\mathbf{t}_i)$$

and the sum of a term and its corresponding inverse in (3·19) is

$$\exp-2\pi i\mathbf{h}^t\mathbf{t}_i+\exp 2\pi i\mathbf{h}^t\mathbf{R}_i^{-1}\mathbf{t}_i\,. \tag{3·20}$$

Now, for the subgroup $\mathbf{R}_i^t\mathbf{h}=\mathbf{h}$, and substitution in (3·20) leads to the expression

$$\exp-2\pi i\mathbf{h}^t\mathbf{t}_i+\exp 2\pi i\mathbf{h}^t\mathbf{R}_i\mathbf{R}_i^{-1}\mathbf{t}_i \tag{3·21}$$

which is a purely real quantity.

Thus we can combine each element in (3·19) with its inverse to give a contribution to the sum which is real; suppose the value of the summation is the real number q. Then (3·19) takes the form

$$pF(\mathbf{h})=qF(\mathbf{h})\,. \tag{3·22}$$

As for lattice absences the only possibilities are that $p=q$ and $F(\mathbf{h})$ is arbitrary, or that $p\neq q$ and $F(\mathbf{h})$ is identically zero. Such a reflexion with zero structure factor is known as a 'space-group absence'.

Equivalent reflexions

We now consider equation (3·19) for the case $\mathbf{R}_i^t\mathbf{h}\neq\mathbf{h}$. We do so by expressing the complex defined by (3·17*a*) as the product of the subgroup defined by (3·17*b*) with the element G_k whose rotation part $\mathbf{R}_k$ appears in (3·18). Thus each term of the complex takes the form

$$(\mathbf{R}_{i'}|\mathbf{t}_{i'})\,(\mathbf{R}_k|\mathbf{t}_k) \tag{3·23a}$$

(where $\mathbf{R}_{i'}=\mathbf{R}_i\mathbf{R}_k$ and $\mathbf{R}_{i'}^t\mathbf{h}=\mathbf{h}$). The product is (equation 1·4*d*)

$$\mathbf{R}_{i'}\mathbf{R}_k|\mathbf{R}_{i'}\mathbf{t}_k+\mathbf{t}_{i'} \tag{3·23b}$$

and the sum in (3·19) is

$$pF(\mathbf{R}_k^t\mathbf{R}_{i'}\mathbf{h})=F(\mathbf{h})\sum_{p\text{ terms}}\exp\{-2\pi i\mathbf{h}^t(\mathbf{R}_{i'}\mathbf{t}_k+\mathbf{t}_{i'})\}\,. \tag{3·24}$$

Applying the result $\mathbf{R}_{i'}^t\mathbf{h}=\mathbf{h}$ to each side we find

$$pF(\mathbf{R}_k^t\mathbf{h})=F(\mathbf{h})\sum_{p\text{ terms}}\exp\{-2\pi i\mathbf{h}^t(\mathbf{t}_k+\mathbf{t}_{i'})\}\,, \tag{3·25a}$$

or, bringing out a factor $\exp(-2\pi i\mathbf{h}^t\mathbf{t}_k)$

$$pF(\mathbf{R}_k^t\mathbf{h})=\exp(-2\pi i\mathbf{h}^t\mathbf{t}_k)\,F(\mathbf{h})\sum_{p\text{ terms}}\exp(-2\pi i\mathbf{h}^t\mathbf{t}_{i'})\,. \tag{3·25b}$$

The summation here is precisely that encountered already in (3·19). As we have shown, its value is purely real. If its value is not equal to p, then $F(\mathbf{h})\equiv 0$, and so therefore does $F(\mathbf{R}_k^t\mathbf{h})$. If the value of the summation is p then

$$F(\mathbf{R}^t\mathbf{h})=\exp\{-2\pi i\mathbf{h}^t\mathbf{t}\,F(\mathbf{h})\} \tag{3·26}$$

even though there are several elements in $\mathscr{G}$ for which $\mathbf{R}_k^t\mathbf{h}=\mathbf{h}$. Physically, the interpretation is that a reflexion whose index $\mathbf{R}^t\mathbf{h}$ can be generated from $\mathbf{h}$ by several different elements in $\mathscr{G}$ can be evaluated as though only one element gave rise to it. Further, it is obvious that if we multiply 3·26 by its complex conjugate then

$$|F(\mathbf{R}^t\mathbf{h})|^2=|F(\mathbf{h})|^2\,. \tag{3·27}$$

i.e. The amplitudes of equivalent reflexions are equal and their relative phases are simply determined.

The multiplicity of a reflexion is the number of different values of $\mathbf{R}^t\mathbf{h}$ generated by the group $\mathscr{G}$. The value of this is determined very simply, as a by-product of the ALGOL procedure 'Generate F' given in the Appendix.

Least-squares refinement

The least-squares method of crystal structure refinement is based on the minimization of a weighted sum of squares of discrepancies between observed structure amplitudes $F_o(\mathbf{h})$, and computed structure factors $F_c(\mathbf{h}, p_i)$ which are functions of n independent parameters $p_i (1 \le i \le n)$. The usual method is to derive corrections δp_i to the parameters by solving the normal equations

$$(\sum_{\mathbf{h}} \mathbf{dd}^t)\,(\delta\mathbf{p}) = (\sum_{\mathbf{h}} \sqrt{\omega}\Delta\mathbf{d}) \qquad (4{\cdot}1)$$

where $\mathbf{d}$ is the vector

$$d_i = \sqrt{\omega}\partial|F_c|/\partial p_i, \qquad (4{\cdot}2)$$

ω is the weight attached to the observation $\mathbf{h}$, Δ is the value of $(|F_o| - |F_c|)$, and the summations are taken over all values of $\mathbf{h}$. This process is applied iteratively, until the refinement is completed.

The formation of the normal equations is carried out on the assumption that each of the p_i is an independent parameter of the problem; if this is the case then the matrix $\sum_{\mathbf{h}} \mathbf{dd}^t$ is necessarily positive definite, and equations (4·1) have a unique solution. However, where atoms occupy special positions in the unit cell some of the p_i are constrained to take arbitrary values, and some may be linear combinations of others. In such cases the matrix is positive semi-definite, and before the equations can be solved the matrix must be modified.

Suppose that a set of independent parameters of the problem is $q_j (1 \le j \le m < n)$, and let

$$\mathbf{p} = \mathbf{Mq} \qquad (4{\cdot}3)$$

define the non-independent parameters $\mathbf{p}$, in terms of $\mathbf{q}$. Now

$$\frac{\partial|F|}{\partial q_j} = \sum_i \frac{\partial|F|}{\partial p_i}\,\frac{\partial p_i}{\partial q_j} \qquad (4{\cdot}4)$$

and from (4·3)

$$\frac{\partial p_i}{\partial q_j} = Mij \qquad (4{\cdot}5)$$

$$\therefore \frac{\partial|F|}{\partial q_j} = \sum_i \frac{\partial|F|}{\partial p_i} Mij \qquad (4{\cdot}6a)$$

or

$$\mathbf{d}_q = \mathbf{M}^t\mathbf{d}_p \qquad (4{\cdot}6b)$$

in an obvious notation. Equations (4·1) for the corrections to the independent parameters now take the form

$$[\sum_{\mathbf{h}}(\mathbf{M}^t\mathbf{d}_p)(\mathbf{M}^t\mathbf{d}_p)^t](\delta q) = \sum_{\mathbf{h}} \sqrt{\omega}\Delta\mathbf{M}^t\mathbf{d}_p \qquad (4{\cdot}7)$$

and the corrections to the non-independent parameters $\mathbf{p}$ are given by

$$\delta\mathbf{p} = \mathbf{M}\delta\mathbf{q}\,. \qquad (4{\cdot}8)$$

It is worth remarking at this stage that $\mathbf{M}$ is a large matrix (n rows and m columns, *i.e.* larger than the reduced set of normal equations). However, $\mathbf{M}$ is very sparse, its non-zero elements are all ratios of small integers, and a suitable ordering of the parameters p_i, q_j in which elements referring to a particular atom in the asymmetric unit form a solid infix* of $\mathbf{p}$, $\mathbf{q}$, allows $\mathbf{M}$ to be bought into a partitioned form with non-trivial blocks on the 'diagonal' ($\mathbf{M}$ is not square) and null blocks elsewhere. Thus the operation suggested by (4·7) is better performed by storing $\mathbf{M}$ as a mapping in the form i, j, M_{ij} than as a straightforward array.

We now show mathematically how to form $\mathbf{M}$; the ALGOL procedure 'make M' given in the Appendix shows how the techniques can be applied in practice.

Coordinate terms

For an atom in a special position the non-independent position parameters $\mathbf{p}$ are represented by $\mathbf{s}$ in (2·7), and the independent parameters $\mathbf{q}$ by $\mathbf{r}$. It follows that in this case

$$\mathbf{p} = 1/h \sum_{\mathscr{H}} G\mathbf{q} = 1/h \sum_{\mathscr{H}} (\mathbf{Rq} + \mathbf{t})\,. \qquad (4{\cdot}9)$$

Obviously

$$\mathbf{p} + \delta\mathbf{p} = 1/h \sum_{\mathscr{H}} G(\mathbf{q} + \delta\mathbf{q}) = 1/h \sum_{\mathscr{H}} (\mathbf{Rq} + \mathbf{t} + \mathbf{R}\delta\mathbf{q}) \qquad (4{\cdot}10)$$

and

$$M_{ij} = \frac{\partial p_i}{\partial q_j} = 1/h \sum_{\mathscr{H}} R_{ij} \quad (1 \le i, j \le 3)\,. \qquad (4{\cdot}11)$$

If, for any j, $M_{ij} \equiv 0$ for all i then the corresponding p_i is obviously constrained to some value governed only by the values of $\mathbf{t}$ in (4·9). It is therefore possible to delete the jth column from $\mathbf{M}$, and the jth element from $\mathbf{q}$, reducing the order of $\mathbf{q}$ by one.

Thermal motion terms

For an atom in a special position the non-independent thermal parameters are represented by $\mathbf{T}$ in (2·13), and the independent parameters by $\mathbf{s}$. In this case therefore

$$\mathbf{T} = 1/h \sum_{\mathscr{H}} \mathbf{RSR}^t \qquad (4{\cdot}12)$$

or, in suffix notation,

$$T_{ij} = 1/h \sum_{\mathscr{H}} R_{ir}R_{js}S_{rs}\,. \qquad (4{\cdot}13)$$

We map T_{ij} on to $p_{(i,j)}$ and S_{rs} on to $q_{(r,s)}$; then

$$p_{ij} = (1/h \sum_{\mathscr{H}} R_{ir}R_{js})\; q_{rs} \qquad (4{\cdot}14)$$

---

* See Iverson (1962).

and the matrix element $M_{(i,\,j),\,(r,\,s)}$ is given by

$$M_{(i,j),(r,s)} = (1/h \sum_{\mathscr{H}} R_{ir} R_{js}) \,. \qquad (4{\cdot}15)$$

Again it will be possible to delete zero columns from $\mathbf{M}$ and reduce the order of $\mathbf{q}$ correspondingly.

Error estimates

The variance-covariance matrix for the parameters $\mathbf{q}$ is given by the inverse of the matrix $\sum_{\mathbf{h}} (\mathbf{M}^t\mathbf{d})\,(\mathbf{M}^t\mathbf{d})^t$ appearing in (4·7). The corresponding matrix for the parameters $\mathbf{p}$, $\sum_{\mathbf{h}} \mathbf{d}\mathbf{d}^t$ is singular, and we cannot form an inverse. We can however form the variance–covariance matrix for the parameters $\mathbf{p}$. Suppose $\bar{q}_i$ is the estimate of the value of the parameter q_i; define a vector $\Delta\mathbf{q}$ by

$$\Delta q_i = q_i - \bar{q}_i \,. \qquad (4{\cdot}16)$$

Then the variance–covariance matrix $\mathbf{Q}$ is defined by

$$\mathbf{Q} = E\{\Delta\mathbf{q}\Delta\mathbf{q}^t\}/N_0 \qquad (4{\cdot}17)$$

where N_0 is the number of degrees of freedom, and E is the expectation operator. Similarly, the variance-covariance matrix for the parameters $\mathbf{p}$ is defined by

$$\mathbf{p} = E\{\Delta\mathbf{p}\Delta\mathbf{p}^t\}/N_0 \,. \qquad (4{\cdot}18)$$

Now

$$\Delta\mathbf{p} = \mathbf{p} - \bar{\mathbf{p}} = \mathbf{M}\mathbf{q} - \mathbf{M}\bar{\mathbf{q}} = \mathbf{M}(\mathbf{q} - \bar{\mathbf{q}}) = \mathbf{M}\Delta\mathbf{q} \,. \qquad (4{\cdot}19)$$

Substituting,

$$\begin{aligned} \mathbf{p} &= E\{(\mathbf{M}\Delta\mathbf{q})(\mathbf{M}\Delta\mathbf{q})^t\}/N_0 && (4{\cdot}20a) \\ &= E\{\mathbf{M}\Delta\mathbf{q}\Delta\mathbf{q}^t\mathbf{M}^t\}/N_0 && (4{\cdot}20b) \\ &= \mathbf{M}(E\{\Delta\mathbf{q}\Delta\mathbf{q}^t\})\mathbf{M}^t/N_0 && (4{\cdot}20c) \\ &= \mathbf{M}\mathbf{Q}\mathbf{M}^t \,, && (4{\cdot}20d) \end{aligned}$$

which allows the computation of $\mathbf{p}$ to be performed.

APPENDIX

The Appendix gives algorithms, in ALGOL 60, for applying the processes described in the text. The actual parameters to be supplied at each procedure activation are described in the comment. For the procedure 'Load cell' the actual array cell must have subscript bounds 1:*P*, 1:3, where *P* > *M*, the number of atoms in the unit cell.

```
real procedure norm(x);
value x; real x;
comment x is normalized so that 0≤x≤1. The non-
    local variable eps specifies the accuracy of work-
    ing;
  norm:=x-entier(x+eps);
real procedure dot (a) times: (b) summed over:(k);
  real a,b; integer k;
comment forms an innerproduct of order 3;
  begin real s; s:=0;
    for k:=1,2,3 do s:=s+a×b;
    dot:=s
  end dot;
boolean procedure equal (a) compared with: (b) over:
    (k,n);
  value n;
  real a,b; integer k,n;
comment equal is true if the two vectors a, b are equal;
  begin boolean s; s:=true;
    for k:=1 step 1 until n do s:=s and abs (a−b)<eps;
    equal:=s
end equal;
procedure apply (R,t,i) the ith operator to: (atom, j)
    the jth atom giving the kth new atom: (new
    atom, k);
  value i, j, k; integer i, j, k;
  array R, t, atom, new atom;
comment on entry i indicates a particular element of
  the space group, which is to be applied to the
  coordinates of the jth atom, stored as x in atom
  [j,1], y in atom [j,2] and z in atom [j,3], so as to
  give the coordinates of the kth new atom;
begin integer p, q;
  for p:=1, 2, 3 do
  new atom [k,p]:=norm (dot(R[i,p,q], atom [j,q],q)+
    t[i,p])
end apply;
procedure Load cell (R,t,N) the space group and
    asymmetric unit: (unit, m) together define the
    contents of the unit cell: (cell, M) and the arrays:
    (tag, check);
  value N, m;
  array R, t, unit cell; boolean array tag;
  integer array check; integer N,m,M;
comment on entry the coordinates of the m atoms in
  the asymmetric unit are in unit, and the N elements of
  the space groups are in R, t. The procedure forms
  the contents of the unit cell in cell, the number of
  atoms being M. The array tag [1:N, 1:M] has
  tag [i,j] true if group element i is a symmetry
  operator for atom j. The array check [1:m] has
  in check [i] the position of the last atom of the
  ith type in the array cell;
begin integer i, j, others, this, element, atom;
  others:=0;
  for atom:=1 step 1 until m do
  begin this:=0; comment number of atoms of this
      type in cell;
    for element:=1 step 1 until N do
    begin apply (R, t, element, unit, atom, cell,
        others+this+1);
      for i:=1 step 1 until this do
      if equal (cell[others+this+1,j], cell[others+
          i,j],j,3)
        then go to special position;
      i:=this:=this+1; comment accept new atom;
```

```
special position: tag[element, others+i]:=true
    end application of all elements to one atom;
  check[atom]:=others:=others+this
  end treatment of all atoms;
  M:=others
end Load cell;
  procedure Generate F(F,m) indices and multiplicity
      for the group: (R,t,N);
    value N;
    array F, R, t; integer m, N;
  comment on entry F[1,1]=h, F[2,1]=k, F[3,1]=l
    and F[4,1], F[5,1] hold the real and imaginary
    parts of F(hkl). The arrays R, t specify the space
    group, of order N. On exit, m gives the number
    of equivalent reflexions, whose indices are in
    F[1,i], F[2,i], F[3,i] and real and imaginary parts
    inF[4,i], F[5,i], (1≤i≤m);
  begin integer i, j, k, arg;
    m:=1;
    for i:=1 step 1 until N do
    begin for j:=1, 2, 3 do F[i,m+1]:=dot (R[i,k,j],
        F[k,1], k);
      for j:=1 step 1 until m do
      if equal (F[k,j], F[k, m+1],k,3) then go to not
        new h;
    new h:m:=m+1;
      arg:=12×norm (dot(F[j,1], t[i,j], j));
      comment form h.t;
      F[4,m]:=F[4,1]×ctab[arg]−F[5,1]×stab[arg];
      F[5,m]:=F[4,1]×stab[arg]+F[5,1]×ctab[arg];
    not new h: end loop for one element
  end Generate F;
procedure make M(M3,M6,t3,t6,R,N,m,tag,check);
  value N,m; integer N,m;
  boolean array t3,t6,tag; integer array check; array
    M3,M6,R;
comment On entry M3[1:3×m,1:3] and M6[1:6×m,
  1:6] contain zeros, the N rotations of the group are
  in R, and tag and check have been initialized by
  load cell. On exit, M3 and M6 hold m 3×3 or 6×6
  blocks of M, one for each atom in the asymmetric
  unit, and non-trivial columns have t3 or t6 false;
begin integer atom, check a,h,p3,p6,element,dp6,q6,i,j;
  for atom:=0 step 1 until m−1 do
  begin loop for one atom: h:=0; p3;=3×atom;
      p6:=6×atom;
    check a:=if atom=0 then 1 else check[atom]+1;
    for element:=1 step 1 until N do
    if tag[element, check a] then
    begin process one element: h:=h+1;
      for i:=1,2,3 do for j:=1,2,3 do
      M3[p3+i,j]:=M3[p3+i,j]+R[element,i,j];
      dp6:=p6;
      for i:=1,2,3 do for j:=i step 1 until 3 do
      begin dp6:=dp6+1; q6:=0;
        for r:=1,2,3 do for s:=r step 1 until 3 do
        begin q6:=q6+1;
          M6[dp6,q6]:=M6[dp6,q6]+R[element,i,r]
            ×R[element,j,s]
        end
      end formation of M6
    end loop for one element;
  for i:=1,2,3 do begin t3[p3+i]:=equal(M3[p3+
        i,j],0,j,3);
      for j:=1,2,3 do M3[p3+i,j]:=M3[p3+i,j]/h
    end normalization of M3;
  for i:=1 step 1 until 6 do
    begin t6[p6+i]:=equal(M6[p6+i,j],0,j,6);
      for j:=1 step 1 until 6 do
        M6[p6+i,j]:=M6[p6+i,j]/h
    end normalization of M6
  end loop for one atom
end make M;
  comment the arrays ctab, stab are declared and
      initialized by;
    array ctab, stab [0:11]; real a; integer i;
      for i:=0 step 1 until 11 do
      begin a:=i×0·5235987756;
        ctab[i]:=cos(a); stab[i]:=sin(a)
      end initialization;
```

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